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## Can or cannot green rust reduce chlorinated ethenes?

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### Abstract

Green rusts (GRs) are  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  layered double hydroxides that are widely investigated for the reduction of inorganic and organic pollutants in soils and groundwaters. Of particular interest is the use of GRs for the reduction of chlorinated ethenes, but existing literature shows contrasting results. Here, we tested 4 GRs (with different interlayer and hydroxide sheet modifications) in reactions with 3 different chlorinated ethenes (tetra-, tri-, and cis-dichloroethylene) for up to 10 months. Our results show that none of the freshly synthesized and untreated GRs can reduce the here tested chlorinated ethenes to any significant extent, corroborated by the lack of degradation products after 10 months and the absence of any significant volatilization. This is in stark contrast to previous literature, which reported that GR can degrade these chlorinated ethenes. The absence of reaction in our experiments is explained by having equilibrated GR suspensions, where the affinity of chlorinated ethenes for GR surfaces is extremely low.

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**Keywords:** green rust; chlorinated solvents; remediation

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### 1. Introduction

Green rusts (GRs) are layered double hydroxides, consisting of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  hydroxide sheets that sandwich interlayer anions (e.g.,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ), water and occasionally monovalent cations [1]. These redox-active compounds form naturally, in iron-rich,  $\text{O}_2$ -poor environments [2,3]. Potentially, they also formed in Precambrian oceans and contributed to banded iron formation 3.8-0.6 billion years ago [4]. Because of GRs' mixed valent character (which most likely allows electron transfer between  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  via small polaron hopping [5]), their high reactive surface area and interlayer ion exchange capacity, GRs are promising, low cost reactants for reduction of inorganic pollutants in soils and groundwaters (e.g.,  $\text{CrO}_7^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ ,  $\text{NpO}_2^+$ ) [6–9]. Additionally, GRs have been suggested

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to be excellent reducing agents for non-polar organic pollutants such as chlorinated hydrocarbons. In particular, several studies have reported significant reduction of chlorinated ethenes (Table 1), such as tetra-, tri and dichloroethenes (PCE, TCE and DCE), which are amongst the most widespread chlorinated solvent pollutants. Thus, GRs could potentially provide a cost-effective approach for soil and groundwater dechlorination. However, reported rates vary in magnitude although the experimental conditions are similar (Table 1). This could be due to different GR synthesis techniques. Alternatively, washing of the GRs is likely to have resulted in partial transformation of GRs to Fe (oxyhydr)oxides (e.g., magnetite, [10]), which could have affected reduction rates.

In this study, we determined the reactivity of freshly synthesized, untreated GRs in experiments with PCE, TCE and cis-DCE. GRs were synthesized by oxidation at constant pH of 7, with either interlayer sulphate (GRSO<sub>4</sub>) or interlayer chloride (GRCl) – see below for synthesis details. In addition, Al-substituted GRs were tested because they have been shown to have lower crystallinity and particles sizes [11,12], which potentially could enhance the number of active surface sites (without reducing the Fe<sup>2+</sup> as an electron source), and therefore reactivity with the chlorinated ethenes.

Table 1. Conditions and derived pseudo-first order rate constants for experiments with GRs and chlorinated ethenes (adapted from [13]). The rate constants were all converted to mass normalized constants using a GR surface area of 20 g/m<sup>2</sup>. The applied molar masses were 779.34 and 430.92 g/mol for GR sulphate (GRSO<sub>4</sub>) and GR chloride (GRCl). The applied Fe<sup>2+</sup>: Fe<sup>3+</sup> was 4:2 for GRSO<sub>4</sub> and 3:1 for GRCl. Rate constant units are expressed as mass loading (g/L) of GR used in reactivity studies.

Chlorinated ethene	Green rust type (synthesis method)	Experimental conditions	Rate constants	Reference
cis-DCE	GRSO <sub>4</sub> (oxidation)	pH 7.7, suspension dilution	9.4 x 10 <sup>-2</sup> L/g/day	[14]
cis-DCE	GRCl (co-precipitation)	suspension dilution	9.24 x 10 <sup>-6</sup> L/g/day	[15]
cis-DCE	GRSO <sub>4</sub> (co-precipitation)	suspension dilution	9.23 x 10 <sup>-6</sup> L/g/day	[15]
cis-DCE	GRSO <sub>4</sub> (oxidation)	pH 7, washed and dried	1.3x10 <sup>-7</sup> L/g/day	[16]
TCE	GRCl (oxidation)	pH 8, washed and dried	1.5x10 <sup>-6</sup> L/g/day	[17]
TCE	GRSO <sub>4</sub> (oxidation)	pH 7, washed and dried	4.2x10 <sup>-6</sup> L/g/day	[16]
PCE	GRSO <sub>4</sub> (oxidation)	pH7, washed and dried	8.1x10 <sup>-6</sup> L/g/day	[16]
PCE	GRCl (oxidation)	pH 8, washed and dried	2.8x10 <sup>-7</sup> L/g/day	[17]

## 2. Methods

### 2.1. Materials and Methods

All stock solutions were prepared using N<sub>2</sub> purged deionized water (MilliQ, 18.3 Ω cm) or methanol in an anaerobic glovebox with the following chemicals: PCE (C<sub>2</sub>Cl<sub>4</sub>, ACS grade ≥ 99%), TCE (C<sub>2</sub>HCl<sub>3</sub>, ACS grade ≥ 99.5%), cis-1,2-DCE (C<sub>2</sub>H<sub>2</sub>Cl<sub>2</sub>, 97%), FeSO<sub>4</sub>•7H<sub>2</sub>O (ACS, ≥ 99%), FeCl<sub>3</sub>•4H<sub>2</sub>O (Reagent plus, 98%), NaOH (ACS, 97%), Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>•12H<sub>2</sub>O (ACS Emsure), AlCl<sub>3</sub>•6H<sub>2</sub>O (Reagent plus, 99%).

### 2.2. GR synthesis and characterisation

GR was synthesized by oxidation of a 50 mM FeSO<sub>4</sub> (for GRSO<sub>4</sub>) or 50 mM FeCl<sub>2</sub> (for GRCl) solution at constant pH 7 using a titrator (Metrohm 785 DMP) equipped with a Ag/AgCl pH-electrode and 1 M NaOH solution. For synthesis of aluminium substituted GRs (Al-GRs), the initial metal concentration was kept constant at 50 mM ([Me]=[Al<sup>3+</sup>] + [Fe<sup>2+</sup>]), while the initial Fe<sup>2+</sup> content was partly replaced by aluminium salts (AlCl<sub>3</sub> or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>) to yield an Al ratio ( $x_{[Al]} = [Al^{3+}] / [Me]$ ) of 0.10. Oxidation and titration was stopped when the total added NaOH volume reached 11 mL in the GRSO<sub>4</sub> synthesis and 6.5 mL in the GRCl synthesis (always completed within an hour), resulting in ~37 mM total [Me] in GR. This was done to avoid pre-mature oxidation of GR to Fe (oxy)hydroxide phases. The resulting blue-green GR suspensions were stirred for an hour prior reduction experiments. X-ray powder diffraction (Bruker D8 Da Vinci XRD, Cu anode: λ = 1.54 Å) was performed on dried solids amended with a thin film of glycerol (to avoid oxidation during measurement) to confirm the formation and purity of GR phases. Transmission electron

microscopy (Phillips CM20, 200 kV) was performed to determine the effect of Al-substitution on particle size and shape.

### 2.3. GR reaction with chlorinated ethenes

Batch experiments to study the reduction of chlorinated ethenes by GR were run in 160 mL serum bottles, with 150 mL of freshly synthesized GR suspension and 10 mL of headspace. PCE, TCE or cis-DCE (pre-diluted in methanol) were added to give final solvent concentrations of 20.6  $\mu\text{M}$ . The serum bottles were immediately capped with a Viton<sup>TM</sup> rubber stopper and crimp sealed. Controls were prepared in degassed MilliQ water. The bottles were placed upside down (to minimize volatilization) on an orbital shaker at 125 rpm. All experiments and controls were run in triplicates. At regular time steps, 1 mL suspension samples were removed from the reactors, mixed with 9 mL of degassed MilliQ water inside a crimped 20 mL glass vial, and then analysed using an Agilent 6890 for headspace gas chromatography mass spectrometry (GC-MS). Prior to headspace extraction, the vials were equilibrated for 15 min at 50°C. One  $\mu\text{L}$  of headspace was injected into a DB-624MS (Agilent) column, with temperature of 35°C and then heated to 115°C at a rate of 10°C/min. External standards were made for every experimental run. To check for degradation products after 10 months of reaction time, 200  $\mu\text{L}$  of headspace from 160 mL serum bottles were manually injected into a Fisher Scientific Trace 1300 gas chromatograph with flame ionization detector and electron capture detector (GC-FID-ECD). The compounds were separated on a porabond U column (Agilent), set at an initial temperature of 40°C and then heated to 260°C at a rate of 10°C/min.

## 3. Results and Discussion

### 3.1. Pure and Al-substituted $\text{GRSO}_4$ and $\text{GRCl}$ synthesis

$\text{GRSO}_4$  and  $\text{GRCl}$  synthesized in the absence of Al ( $x_{[\text{Al}]} = 0$ ; Fig. 1a) showed the typical basal plane reflections of these layered materials, with  $d_{(001)} = 10.91 \text{ \AA}$  ( $\text{GRSO}_4$ ) and  $d_{(003)} = 7.90 \text{ \AA}$  ( $\text{GRCl}$ ), as reported previously for these compounds [18]. The differences in basal plane spacing are due to the different size and arrangement of the interlayer ions [19]. In addition to different basal plane spacing,  $\text{GRCl}$  also exhibited broader basal peaks (Fig. 1a), indicating smaller crystallite sizes. This is also supported by TEM observations, showing that  $\text{GRCl}$  particles are 2–10 times smaller in size, and more rounded, compared to  $\text{GRSO}_4$  particles (Fig. 1b, d).

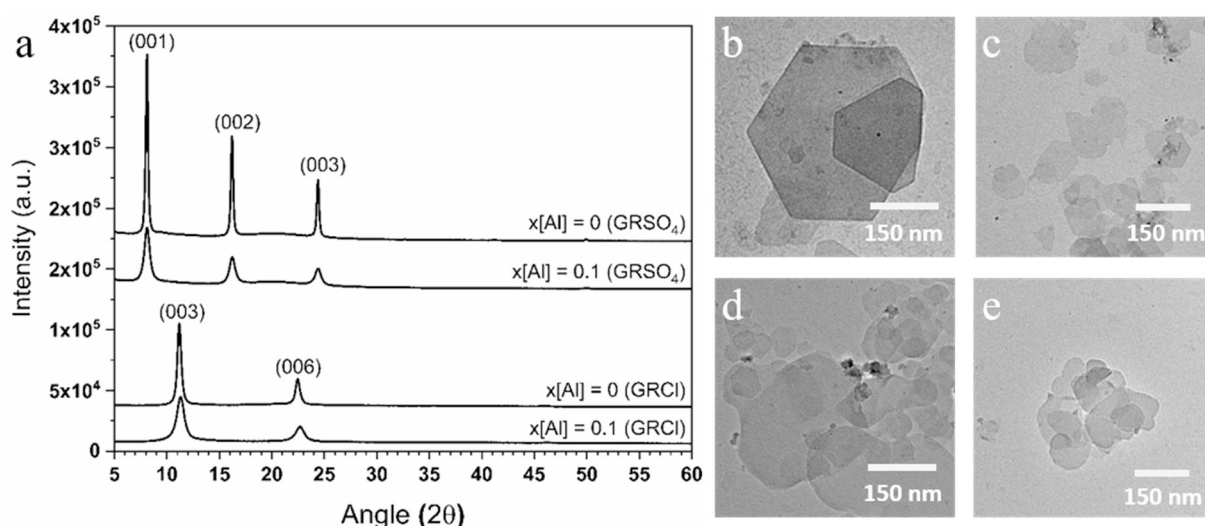


Fig. 1. (a) XRD of  $\text{GRSO}_4$  and  $\text{GRCl}$  synthesised in the absence (pure) and presence of Al ( $x_{[\text{Al}]} = 0.1$ , Al-GR). Peaks are annotated with Miller indices. TEM images of (b) pure  $\text{GRSO}_4$ , (c) Al- $\text{GRSO}_4$ , (d)  $\text{GRCl}$ , and (e) Al-  $\text{GRCl}$ , showing variations in crystal morphology and size. Small, high contrast, spherical particles are magnetite crystals that most likely formed during sample preparation for TEM.

Al-GRSO<sub>4</sub> and Al-GRCl ( $x_{[Al]} = 0.1$ ; Fig. 1a) showed similar basal plane spacing as their pure counterparts, but peaks were slightly shifted to lower d-values (e.g.,  $d_{001} = 10.89 \text{ \AA}$  for Al-GRSO<sub>4</sub> and  $d_{003} = 7.82 \text{ \AA}$  for Al-GRCl). These peak shifts are best explained by the higher ionic potential of Al<sup>3+</sup> compared to Fe<sup>3+</sup> ( $r_{Fe^{3+}} = 0.65 \text{ \AA}$ ,  $r_{Al^{3+}} = 0.53 \text{ \AA}$ ) [19], resulting in tighter bonds within the hydroxide layer, and thus a contraction in the basal plane spacing. Additionally, the XRD peaks broadened (Fig. 1a), implying that the crystallinity in Al-substituted GRs was lower compared to the pure GRs. This is also consistent with the TEM images (Fig. 1c, e) where the GR sheets appeared more rounded (change in morphology) and thinner (change in contrast) relative to pure GRs. A similar decrease in basal plane spacing and decrease in crystallinity due to Al incorporation were also reported for Al-GRSO<sub>4</sub> synthesised by co-precipitation [20]. Al-substitution in GRCl has not been yet reported but the change in average structure is similarly affected as in GRSO<sub>4</sub>.

### 3.2. GR reactivity with chlorinated ethenes

Three types of chlorinated ethenes (i.e., PCE, TCE, cis-DCE) were reacted with the pure and Al-substituted GRSO<sub>4</sub> and GRCl over 90 days. Within the uncertainty of the measurements, both control and GR reduction experiments exhibited the same concentrations of ethenes after 90 days as were added at the beginning of each experiment (Fig. 2). This means that no reduction was detected in any of the experiments over this time span, not even for Al-GR, where particle size and crystallinity was substantially lower. These results contradict previous studies that showed significant reduction of PCE, TCE and cDCE by GRSO<sub>4</sub> and GRCl within 60–70 days [16,17] (Table 1). Potentially, the contrast in results could be caused by differences in experimental procedures (e.g., solution pH, and synthesis protocols). For example, here the synthesized GRs were not washed and dried, or re-diluted prior to reduction experiments. We purposely avoided these post-synthesis treatments to ensure that GRs did not transform. Differences could also have resulted from the use of different sized batch reactors and different solution-volume to headspace ratio because these factors highly affect volatilization and/or partitioning of the chlorinated solvents. In particular, these effects increase with increasing halogenation of the chlorinated ethenes (e.g. halogenation: PCE > TCE > cis-DCE) [21]. Thus, potential errors due to partitioning and volatilization would be expected to be highest for experiments performed with PCE in small reactor volumes with a large headspace volume. In this study, a large reactor volume (160 mL) and small headspace volume (10 mL) was used to assure negligible volatilization and increased sensitivity of GC measurements.

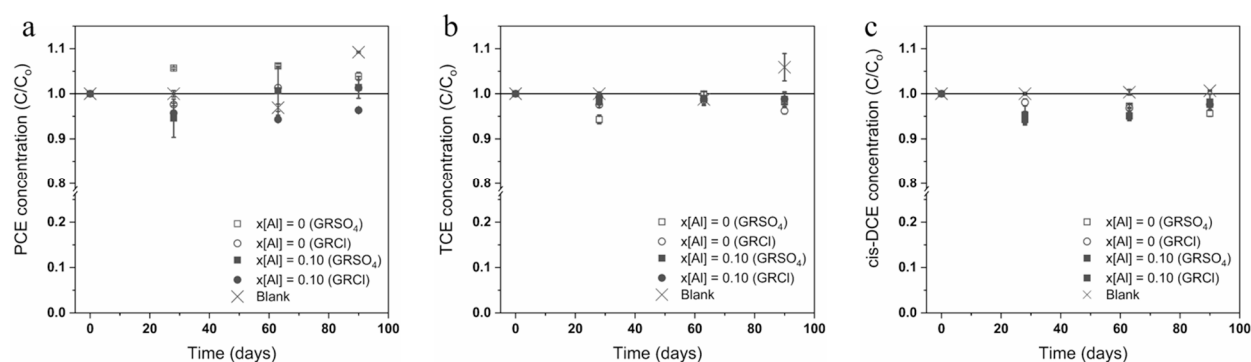


Fig. 2. Evolution of the concentrations of (a) PCE, (b) TCE and (c) cis-DCE in control and reduction experiments with pure and Al-substituted ( $x_{[Al]} = 0.1$ ) GRSO<sub>4</sub> and GRCl. The plots oscillate at  $C/C_0 = 1$ , implying undetectable chlorinated ethene reduction.

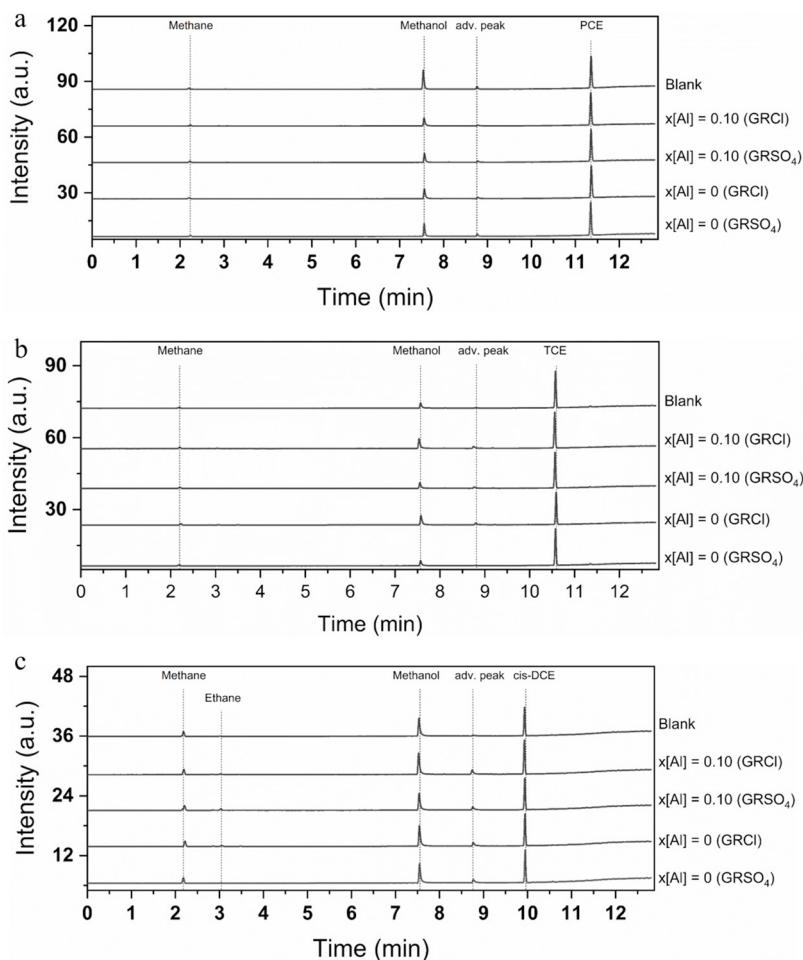


Fig. 3. Plots of FID spectra from headspace analyses of reduction experiments after 10 months to identify possible degradation end-products in reactions with pure and Al-substituted GRs and (a) PCE, (b) TCE and (c) cis-DCE.

To assess the long-term reduction of chlorinated ethenes by GRs, the batch reactors were left to react for another 7 months in the dark. FID spectra of headspace samples removed after 10 months showed intense peaks of PCE, TCE and cis-DCE in similar quantities as the blank control (Fig. 3). The only reduction experiments that showed tiny amounts of degradation products, i.e., ethane (retention time between 2-3 min, Fig. 3), were GRs exposed to cis-DCE. However, these quantities are orders of magnitude smaller than expected from the reduction kinetics reported in previous studies (Table 1). Again, no differences in reactivities were seen between pure and Al-substituted GRs. Thus, we conclude that chlorinated ethenes were not reduced to any significant extent by the pure and Al-substituted GRs tested here.

#### 4. Conclusion

This study investigated the reactivity of GRs prepared with different interlayer anions (sulphate and chloride), and with/without Al-substitution in the hydroxide layer, towards degradation of chlorinated ethenes (e.g. PCE, TCE, and cis-DCE). The synthesized GRs were not washed nor dried prior experiments to minimise its dissolution and transformation to other Fe oxyhydroxide phases. Contrary to previous literature, no significant reduction of the chlorinated ethenes could be detected, even after 10 months. This raises the questions as to how GR reactivity can be so dramatically different between studies. Post-treatments such as washing and drying of GR could potentially explain the discrepancy, because such treatments could affect GR structure and favour the formation of minerals that may

reduce the chlorinated ethenes. From the experiments performed here, GR would be a poor candidate for chlorinated ethene reduction. However, it would be worth investigating what happens to GR interfaces when diluted, washed, or dried to better understand previously reported observations.

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